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(54) MOISTURE-CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a modified silicone moisture-curable composition which has a high curing rate and uses a catalyst system having a low toxicity.

SOLUTION: The moisture-curable composition contains a mixed catalyst comprising from 0.1 to 10 pts.wt. bismuth compound (B) and a reaction product obtained by allowing, based on 1 mol bismuth compound (B), from 1 to 7 mol, calculated as the molar number of carboxyl groups, compound (C) having at least one carboxyl group to react with from 0.6 to 3.5 mol, calculated as the molar number of amino groups, compound (D) having at least one amino group as a curing catalyst against 100 pts.wt. silyl group-containing organic polymer (A) having at least one hydrolyzable group-bound silicon atom at the molecular terminal or the side chain.

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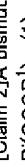
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CLAIMS

[Claim(s)]

[Claim 1] As opposed to sil group content organicity polymer (A) 100 weight section which has the silicon atom combined with a molecular terminal or a side chain with a hydrolytic basis in [at least one] one molecule, as a curing catalyst — the bismuth compound (B) 0.1 – ten weight sections — and, Based on quantity of 1 mol of a bismuth compound (B), A carboxyl group, A compound (C) which it has at least one piece. A wet cure type composition containing a mixed catalyst which consists 0.6~3.5 mol of a reactant produced by making react based on the number of mols of an amino group in a compound (D) which has 1~7 mol and at least one amino group based on the number of mols of a carboxyl group.

[Claim 2] A bismuth compound (B) is a general formula (1).



The wet cure type composition according to claim 1 which is bismuth carboxylate expressed with (inside of formula and R' is a hydrocarbon group of the carbon numbers 1~17).

[Claim 3] The wet cure type composition according to claim 1 or 2 whose bismuth compound (B) is bismuth tris (2-ethylhexanoate) or bismuth tris (neo decanoate).

[Claim 4] The wet cure type composition according to any one of claims 1 to 3 whose compound (C) which has at least one carboxyl group is straight chain or branched-chain aliphatic carboxylic acid of saturation of the carbon numbers 2~18, or an unsaturation.

[Claim 5] The wet cure type composition according to any one of claims 1 to 4 whose compound (D) which has at least one amino group is primary amine.

[Claim 6] A mixed catalyst to a bismuth compound (B) based on quantity of 1 mol of a bismuth compound (B), A reactant produced [mol] by making 1~3 mol react based on the number of mols of an amino group in a compound (D) which has 2~5 mol and at least one amino group for a compound (G) which has at least one carboxyl group based on the number of mols of a carboxyl group is blended. The becoming wet cure type composition according to any one of claims 1 to 5.

[Translation done.]

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DETAILED DESCRIPTION

Detailed Description of the Invention

[0001]

[Field of the Invention]The cure rate of this invention is quick and it relates to the wet cure type composition which uses few toxic catalyst systems.

[0002]

[Description of the Prior Art]As moisture curing nature rubber, silicone rubber, urethane rubber, polysulfide rubber, etc. are known from the former.

[0003]However, silicone series rubber has a problem in respect of the possibility of the contamination to the circumference, and the paintwork to the surface, and urethane system rubber has a problem in respect of storage stability, weatherability, fizz-proof, discoloration, etc. There is a problem in respect of hardenability and the possibility of the contamination to the circumference also about polysulfide system rubber.

[0004]Modified silicone system rubber is a polymer which has a hydrolytic silicon functional group which uses polyether etc. as a main chain, and for which a bridge can be constructed. Although it is stability under seal for a long period of time using a curing catalyst, if it exposes to humidity, it is used as a liquid setup-of-tooling product which hardens quickly and changes to a rubber-like substance (JP,62-35421,B, JP,61-141761,A, JP,1-58219,A).

This polymer has storage stability, weatherability, fizz-proof, and good allochroism compared with a polyurethane system, compared with a polysulfide system, it excels in hardenability, there is little stain resistance to the circumference, and there is no toxicity. There is little stain resistance to the circumference compared with the usual silicone series, and the paintwork to the surface is good. Although a titan compound, a tin carboxylate compound, a lead carboxylate compound, etc. are known as a curing catalyst of the polymer which has this hydrolytic silicon functional group, The cure rate of a titanium compound is not enough, and since the load to environment is large, when using it, sufficient cautions are [organic lead compounds and organic tin compound] needed. Although it is JP,8-41358,A news and using a bismuth compound with few problems of safety is proposed by the concomitant use catalyst of carboxylic acid and amine, and JP,5-34928,A news as a hardening setup-of-tooling product which does not use a substance with **** of such environmental pollution, A cure rate is unsatisfying practical.

[0005] [Problem(s) to be Solved by the Invention]In view of the problem of said conventional technology, the cure rate of this invention is quick and it makes it SUBJECT to provide the denaturation silicone series wet cure type composition which uses few toxic catalyst systems.

[0006]

[Means for Solving the Problem]Namely, an invention concerning claim 1 receives a molecular terminal or a side chain at silyl group content organicity polymer (A) 100 weight section which has the silicon atom combined with a hydrolytic basis in [at least one] one molecule, as a curing catalyst --- the bismuth compound (B), A carboxyl group. A compound (C) which it has at least one piece. It is related with a wet cure type composition containing a mixed catalyst which consists 0.6-3.5 mol of a reactant produced by making react based on the number of mols of an amino group in a compound (D) which has 1-7 mol and at least one amino group based on the number of mols of a carboxyl group.

[0007]In an invention concerning claim 2, a bismuth compound (B) is a general formula (1).

$\text{Bi}(\text{OCOR}')_3$ (1)

It is related with the wet cure type composition according to claim 1 which is bismuth carboxylate expressed with (inside of formula and R' is a hydrocarbon group of the carbon numbers 1~17).

[0008]An invention concerning claim 3 relates to the wet cure type composition according to claim 1 or 2 whose bismuth compound (B) is bismuth tris (2-ethylhexanoate) or bismuth tris (neo decanoate).

[0009]An invention concerning claim 4 relates to the wet cure type composition according to any one of claims 1 to 3 whose compound (C) which has at least one carboxyl group is straight chain shape or branched-chain aliphatic carboxylic acid of saturation of the carbon numbers 2~18, or an unsaturation.

[0010]An invention concerning claim 5 relates to the wet cure type composition according to any one of claims 1 to 4 whose compound (D) which has at least one amino group is primary amine.

[0011]A mixed catalyst: an invention concerning claim 6 to a bismuth compound (B) based on quantity of 1 mol of a bismuth compound (B). A reactant produced [mol] by making 1~3 mol react based on the number of mols of an amino group in a compound (D) which has 2~5 mol and at least one amino group for a compound (C) which has at least one carboxyl group based on the number of mols of a carboxyl group is blended. It is related with the becoming wet cure type composition according to any one of claims 1 to 5.

[0012] [Embodyment of the Invention]The silicon atom which combined with the molecular terminal or the side chain the organic polymer (A) used for this invention with the hydrolytic basis, It is a silyl group content organicity polymer which it has [(it may be hereafter called the silicon group combined with the hydrolytic basis) and] in [at least one] one molecule, and an alkylene oxide polymer thru-/or polyether, an ether ester block copolymer, etc. are raised as the main chain. The polymer of an ethylenic unsaturated compound and diene series, etc. are raised.

[0013]As said alkylene oxide polymer thru-/or polyether, what has repeating units, such as n ($\text{CH}_2\text{CH}_2\text{O}$)_n($\text{CH}_3\text{CH}_2\text{O}$)_n($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$)_n($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$)_n is illustrated. n is two or more integers here.

[0014]As a polymer of an ethylenic unsaturated compound and diene series, Homopolymers, such as ethylene, propylene, acrylic ester, methacrylic acid ester, vinyl acetate, acrylonitrile, styrene, isobutylene, butadiene, isoprene, and chloroprene, or two or more sorts of these copolymers are raised. More specifically Polybutadiene, a styrene butadiene copolymer, An acrylonitrile butadiene copolymer, an ethylene-butadiene copolymer, Ethylene propylene rubber, an ethylene-vinylacetate copolymer, an ethylene-acrylic ester copolymer, Polyisoprene, a styrene isoprene copolymer, Polyisobutylene-isoprene copolymer, Polychloroprene, a styrene chloroprene copolymer, an acrylonitrile chloroprene copolymer, polyisobutylene, polyacrylic ester, polymethacrylic acid ester, etc. are raised.

[0015]The silicon group combined with the hydrolytic basis is a basis which causes a condensation reaction by using a catalyst etc. if needed under existence of humidity and a cross linking agent. Specifically, a halogenation silyl group, alkoxy silyl groups, an oxime oxysilyl group, an amine oxysilyl group, an amino silanol group, an amine silanol group, an amine silanol group, etc. are raised. Here, the number of these hydrolytic bases combined with one silicon atom is chosen from the range of 1~3. The number of the hydrolytic bases combined with one silicon atom may be one, and that of them may be [two or more]. Furthermore, the hydrolytic basis and the non-hydrolytic basis may combine with one silicon atom. As a silicon group combined with the hydrolytic basis, handling is an easy point, and especially alkoxy silyl groups (mono- alkoxy silyl groups, a dialkoxy silyl group, and the Tori alkoxy silyl groups are included) is preferred. The silicon group combined with the hydrolytic basis may exist in the end of a polymer molecule, or may exist in the side chain. Even if the silicon group combined with the hydrolytic basis has few polymers per molecule, it is preferred that it averages per molecule from a point of a cure rate and hardened material nature, and there are 1.5 or more pieces with one piece although it is good. A method publicly known as a method of combining with said main chain polymer the silicon group combined with the hydrolytic basis is employable.

[0016]Although the molecular weight of the organic polymer (A) used by this invention does not have

restrictions in particular, the thing of polymers is hyperviscosity, and since it becomes difficult [a use top] when it is considered as a hardening setup-of-tooling product, 30000 or less are too desirable [a thing] as a number average molecular weight. Although such an organic polymer can be manufactured by a publicly known method, commercial items, such as KANEKA MS polymer by Kaneka Corp., may be used for it.

[0017]As a bismuth compound (B) used for this invention, one sort of the bismuth SUTORI carboxylate expressed with said general formula (1) or two sorts or more are used preferably. As carboxylic acid of the carbon numbers 2-18 which give the carboxyl group shown by OGOR1 in a general formula (1), Acetic acid, propionic acid, butanoic acid, isobutanoic acid, pentanoic acid, hexanoic acid, pentanoic acid, Octanoic acid, 2-ethylhexanoic acid, nonanoic acid, decanoic acid, neo decanoic acid ($\text{CH}_3(\text{CH}_2)_5\text{C}(\text{CH}_3)_2\text{COOH}$). The straight chain shape or the branched-chain aliphatic carboxylic acid of saturation, such as lauric acid, myristic acid, palmitic acid, stearic acid, and oleic acid, or an unsaturation is raised. If the bismuth SUTORI carboxylate expressed with a general formula (1) is illustrated concretely, Bismuth triacetate, bismuth tripionate, bismuth heptanoate, Screw mast RIOKUNOETO, bismuth tris (2-ethylhexanoate), bismuth tris (neo decanoate), bismuth trilaurate, a bismuth trio rate, bismuth tristearate, etc. are raised. Bismuth tris (2-ethylhexanoate) and bismuth tris (neo decanoate) are [among these] preferred. Such a compound can be manufactured by a publicly known method.

[0018]As the compound (C), which has at least one carboxyl group, and (calling it carboxyl containing compound (C) hereafter), one sort of the straight chain shape of the saturation of the carbon numbers 2-18 or an unsaturation or branched-chain aliphatic carboxylic acid or two sorts or more are used preferably. When it illustrates concretely, acetic acid, propionic acid, hexanoic acid, octanoic acid, Saturation, unsaturation aliphatic dicarboxylic acid, etc., such as unsaturation aliphatic carboxylic acid, such as saturated-fat follows carboxylic acid, such as 2-ethylhexanoic acid, neo decanoic acid, lauric acid, and stearic acid, oleic acid, linoleic acid, and arachidonic acid, fumaric acid, and maleic acid, are raised. The saturated-fat follows carboxylic acid of the carbon numbers 8-12 of octanoic acid, 2-ethylhexanoic acid, lauric acid, etc. is preferred, and 2-ethylhexanoic acid and especially neo decanoic acid are [among those] preferred.

[0019]As *** (D) which has at least one amino group, and (calling it hereafter amino group containing compound (D)), primary amine is used preferably. When it illustrates concretely, as primary amine Methylamine, ethylamine, Propylamine, isopropylamine, isobutylamine, 1-ethyl butylamine, isobutyl amine, pentylamine, To neo, PUCHIRU amine, octylamine, neo decyl amine, lauryl amine, Monoethanolamine, diethylamino propylamine, oleylamine, Cyclohexylamine, benzylamine, Guanidine, 2-ethylhexylamine, Diethyltetraamine, aniline, a nitroaniline, Aromatic primary amine, such as triethylenetetramine, aniline, toluidine, tolyl amine, xylylamine, a 2,3-xylidine, an anisidine, phenetidine, benzylamine, and naphthylamine, is raised. Octylamine, neo decyl amine, lauryl amine, 2-ethylhexylamine, and benzylamine are [among these] preferred, and lauryl amine and especially 2-ethylhexylamine are preferred.

[0020]Before adding to a sily group content organicity polymer (A), it is necessary to make a carboxyl containing compound (C) and an amino group containing compound (D) react mutually enough a priori in the hardening setup-of-tooling product, of this invention. It may mix at once and a carboxyl containing compound (C) and an amino group containing compound (D) may be made to react at this time. An amino group containing compound (D) may be made to add and react to a carboxyl containing compound (C), and a carboxyl containing compound (G) may be made to add and react to an amino group containing compound (D). A reaction is performed usually stirring both mixed liquor (when a mixture is not liquefied, it heats, and is made liquefied or a meltable solvent is added) under the absence of a solvent. A reaction must be thoroughly performed until reaction fever stops occurring.

[0021]The mixed catalyst used for this invention may add and prepare a bismuth compound (B) to the reactant of the above-mentioned carboxyl containing compound (C) and an amino group containing compound (D). An amino group containing compound (D) is added into the mixture of a bismuth compound (B) and a carboxyl containing compound (C), and under existence of a bismuth compound (B), a carboxyl containing compound (C) and an amino group containing compound (D) may be made to react, and it may prepare. A carboxyl containing compound (G) is added into the mixture of a

bismuth compound (B) and an amino group containing compound (D), and under existence of a bismuth compound (B), a carboxyl containing compound (C) and an amino group containing compound (D) may be made to react, and it may prepare. A bismuth compound (B), a carboxyl containing compound (C) and an amino group containing compound (D) may be made to react, and it may prepare.

[0022]In the hardening setup-of-tooling product of this invention, the content of a bismuth compound (B) has 0.1 - 10 preferred weight section to sily group content organicity polymer (A) 100 weight section. When said less than range of hardening performance is [the quantity of a bismuth compound (B)] insufficient and it exceeds said range on the other hand, physical properties, such as recovery of the hardened material after hardening and weatherability, may worsen. The content of a carboxyl containing compound (G), Based on the number of mols of a carboxyl group, to the quantity of 1 mol of a bismuth compound (B), 2-5 mol, preferably, are 3 mol most preferably more preferably [1-7 mol is preferred and], and 3-4 mol especially the content of an amino group containing compound (D), 2-3 mol 1-3 mol is 2 mol most preferably especially more preferably [0.6-3.5 mol is preferred to the quantity of 1 mol of a bismuth compound (B), and]. If said less than range of hardening performance is [the content of a carboxyl containing compound (C)] insufficient and it exceeds said range on the other hand, hardening performance degradation will be seen. If said less than range of hardening performance is [the content of an amino group containing compound (G)] insufficient and it exceeds said range on the other hand, hardening performance degradation will be seen.

[0023]In order to promote hardening in the moisture constituent of this invention and to improve adhesion to a substrate, can use publicly known various amino group substitution alkoxysilane compounds or the condensate of those, and specifically, gamma **AMINO propyl trimethoxysilane, N-(trimethoxysilyl)propyl propyl(trimethoxysilane, gamma **AMINO propyl triethoxysilane, N-(trimethoxysilyl)propyl) ethylenediamine, delta-aminobuty (methyl) diethoxysilane, N, and N **BISU (trimethoxysilyl)propyl ethylene diamine, these partial hydrolysates, etc. are raised.

[0024]The additive agent usually further added by hardenability constituents, such as a bulking agent, colorant, a plasticizer, a hardening accelerator, a concrete retarder, a dripping inhibitor, an antiaging agent, and a solvent, may be added to the moisture curing nature constituent of this invention. As a bulking agent, specifically For example, calcium carbonate, kaolin, talc, Fumed silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, clay, Calcination clay, glass, bentonite, organic bentonite, a melt balloon, glass fiber, asbestos, a glass filament, grinding quartz, diatomite, aluminum silicate, aluminium hydroxide, a zinc oxide, magnesium oxide, a titanium dioxide, etc. are raised. Specifically as colorant, iron oxide, carbon black, copper phthalocyanine blue, Phthalocyanine Green, etc. are used. As a plasticizer, specifically Dibutyl phthalate, diethyl phthalate, Phthalic ester, such as butylbenzyl phthalate, diethyl adipate, Succinic acid diethyl, succinic acid disodioyleate, diisodecyl sebacate, Glycol ester, such as aliphatic-carboxylic-acid ester species, such as trioctyl phosphate and triresyl phosphate, epoxy plasticizers, such as phosphoric ester, such as trioctyl chlorinated paraffin, etc. are used. Specifically as a dripping inhibitor hydrogenation castor oil, a silicic acid anhydride, organic bentonite, colloidal silica, etc. are used. As other additive agents, adhesion grant agents, such as phenol resin and an epoxy resin, an ultraviolet ray absorbent, radical chain inhibitor, a peroxide decomposition agent, various kinds of antiaging agents, etc. are used.

[0025] [Example] although this invention is concretely explained based on an example below, the range of this invention be elaborate — be alike — *** is not limited.

[0026]In the attached 200-ml eggplant type flask, an example of manufacture 1 nitrogen introducing pipe 43 g (0.3 mol) of 2-ethylhexanoic acid, 37.0 g (0.2 mol) of lauryl amine and 63.9 g (0.1 mol) of bismuth tris (2-ethylhexanoate) were weighed, and it fully mixed with the magnetic stirrer. Generation of heat was subsided, stirring was continued until the internal temperature became near the room temperature, and the fluid of yellow transparency was obtained.

[0027]In the attached 200-ml eggplant type flask, an example of manufacture 2 nitrogen introducing pipe 43.3 g (0.3 mol) of 2-ethylhexanoic acid, After weighing 63.9 g (0.1 mol) of bismuth tris (2-ethylhexanoate) and fully mixing with a magnetic stirrer, 37.0 g (0.2 mol) of lauryl amine was added to react, and it may prepare. A carboxyl containing compound (G) is added into the mixture of a

and agitated. Generation of heat was subsided, stirring was continued until the internal temperature became near the room temperature, and the fluid of yellow transparency was obtained.

[0028] In the attached 200-ml eggplant-type flask, an example of manufacture 3 nitrogen introducing pipe 37.0 g (0.2 mol) of laurylamine. After weighing 63.9 g (0.1 mol) of bismuth tris (2-ethylhexanoate) and fully mixing with a magnetic stirrer, 43.3 g (0.3 mol) of 2-ethylhexanoic acid was added and agitated. Generation of heat was subsided, stirring was continued until the internal temperature became near the room temperature, and the fluid of yellow transparency was obtained.

[0029] By the mole ratio shown in Table 1 like the example 4 of manufacture - the example 1 of 20 manufactures, a bismuth compound (B), Mix, a carboxylic containing compound (C), (2-ethylhexanoic acid and neo-decanoic acid), an amino group containing compound (D), and (lauryl amine and 2-ethylhexylamine) were made to react, and the mixed catalyst was prepared.

[0030] To Example 1 – 12 silyl-group content organicity polymer (MS polymer S303 by Kaneka Corp.) 100 weight section, it was shown in Table 2, and quantity (weight section) addition was carried out, the mixed catalyst acquired in the examples 1 – 12 of manufacture was kneaded, and the hardening setup-of-tooling product was prepared.

[0031] To the comparative example 1 – 8 silyl-group content organicity polymer (MS polymer S303 by Kaneka Corp.) 100 weight section, it was shown in Table 3, and quantity (weight section) addition was carried out, the mixed catalyst acquired in the examples 13 – 20 of manufacture was kneaded, and the hardening setup-of-tooling product was prepared.

[0032] About the obtained hardening setup-of-tooling product, a snap time (time until it half-gels and mobility is lost), and tack free time (time until surface tackiness is lost) were measured. Operation from kneading to hardening was performed in the thermostatic chamber of the room temperature of 23 **, and 60% of humidity RH A result is shown in Tables 2 and 3.

[Table 1]
Table 1

試験混合比(モル)	
製造例1	1
製造例2	1
製造例3	1
製造例4	1
製造例5	1
製造例6	1
製造例7	1
製造例8	1
製造例9	1
製造例10	1
製造例11	1
製造例12	1
製造例13	1
製造例14	1
製造例15	1
製造例16	1
製造例17	1
製造例18	1
製造例19	1
製造例20	1

1) H系化物(液体)型
2) COMICAL社製

[Table 2]
Table 2

http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web.cgi_ejje?atw_u=http%3A%2F%2Fwww4.ipdl.i... 2010/03/03
http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web.cgi_ejje?atw_u=http%3A%2F%2Fwww4.ipdl.i... 2010/03/03

表 2	
混合触媒	比較例1 製造例1 製造例2 製造例3 製造例4 製造例5 製造例6 製造例7 製造例8 製造例9 製造例10 製造例11 製造例12
触媒量(g)	6.5 6.5 6.5 6.5 6.5 6.5 6.5 6.5 6.5 6.5 6.5 6.5
ストップ4.6(min)	25 27 24 32 25 28 20 25 28 24 23 28
タクツリ-9.1(min)	170 175 170 185 175 180 185 170 175 170 175 180

[Table 3]
Table 3

表 3	
混合触媒	比較例1 製造例1 製造例2 製造例3 製造例4 製造例5 製造例6 製造例7 製造例8 製造例9 製造例10 製造例11 製造例12
触媒量(g)	5.3 5.3 5.3 5.3 5.3 5.3 5.3 5.3 5.3 5.3 5.3 5.3
ストップ4.6(min)	73 60 61 40 40 40 40 40 40 40 40 40
タクツリ-9.1(min)	300 280 280 200 200 200 200 200 200 200 200 200

[0035]
[Effect of the Invention]The wet cure type composition using the specific curing catalyst of this invention has a quick cure rate compared with the conventional constituent, and such a wet cure type composition is useful as a sealing agent, a coating agent, and elastic adhesives so that clearly from Tables 2 and 3.

[Translation done.]